Shape-controlled synthesis of silver sulfide nanocrystals by understanding the origin of mixed-shape evolution†

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The shape of silver sulfide nanomaterials was successfully controlled by understanding the origin of the mixed-shape problem.

The shape-controlled synthesis of semiconductor nanoparticles has been extensively studied in an attempt to discover unprecedented shape-dependent physical properties.[1] For example, one-dimensional cadmium selenide nanomaterials show interesting shape effects in their optical properties, and cadmium selenide nanorods and nanospheres show linearly and circularly polarized emissions, respectively.[2] Thus, diverse synthetic routes to these nanomaterials have been actively developed during the last decade. The influence of several experimental conditions, including the concentration of precursors and reaction temperature, on the resultant shape of nanomaterials is well recognized, and the use of suitable ligands can also induce the evolution of shape by selectively blocking certain crystalline planes of the growing nanomaterials.[3]

One of the notorious problems in the shape-controlled synthesis of metal chalcogenide nanomaterials is the mixed-shape of the synthesized materials. There have been a significant number of reports on the synthesis of semiconductor nanomaterials of mixed-shape.[4] For example, the synthesis of nickel sulfide nanomaterials showed the formation of a mixture of two-dimensional plates and one-dimensional rod nanomaterials.[5] In a recent study, we also experienced the mixed-shape problem in the wet chemical synthesis of non-spherical silver sulfide nanomaterials, as shown in Fig. 1a.[6]

The goal of this work is to disclose the origin of the mixed-shape problem and to prepare uniform-shaped anisotropic silver sulfide nanomaterials, since accomplishing this should be very helpful in the shape-controlled synthesis of diverse semiconductor nanoparticles. In a typical synthesis, anhydrous silver nitrate (50 mg, 0.29 mmol) was used as the silver source and was dissolved in 2 mL of oleylamine by the application of an appropriate amount of heating under argon. It is noteworthy that the silver salt itself has a very low solubility in the relatively non-polar oleylamine. Thus, the dissolution seemed to result from the coordination of amine to silver, which forms somewhat less polar complexes. Usually, the solution that formed had a reddish-yellow color, as shown in Fig. 1b. The reaction of this solution with five equivalents of elemental sulfur in 5 mL of oleylamine at 100 °C formed a black solution. Quenching this solution with excess methanol resulted in the precipitation of a black powder. Transmission electron microscopy (TEM) analysis showed a mixture of ~20 nm-sized particles, and rods having a width of ~12 nm and length of ~43 nm. At first, we speculated about the possibility of an oriented attachment mechanism of spherical nanoparticles to form rods.[8] However, it was observed that the use of a prolonged reaction time did not induce the anisotropic growth of spherical nanoparticles. Moreover, there is a significant difference between the diameter of the particles and the width of the rods, as shown in Fig. 1a. This implies that the two kinds of shaped nanomaterials were formed independently.

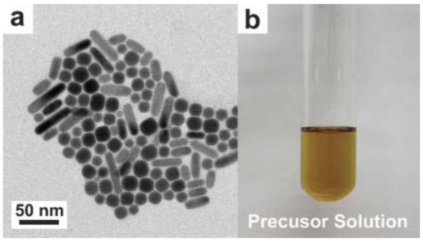

Fig. 1 (a) Example of the mixed-shape problem and (b) precursor solution used[7] in the synthesis of silver sulfide nanomaterials.

Unexpectedly, after many unsuccessful attempts to prepare uniform-shaped non-spherical nanomaterials, we found that the silver nitrate can be very slowly dissolved in oleylamine at a relatively low temperature, even at room temperature. Usually, it took around 1 h to dissolve 50 mg of silver nitrate in 2 mL of oleylamine with the help of sonication at room temperature (solution **A** in Fig. 2). Very interestingly, the solution has a pale yellow color, as shown in Fig. 2.

It is very important to keep the temperature sufficiently low to obtain a pale yellow solution. In contrast, sufficient heating of

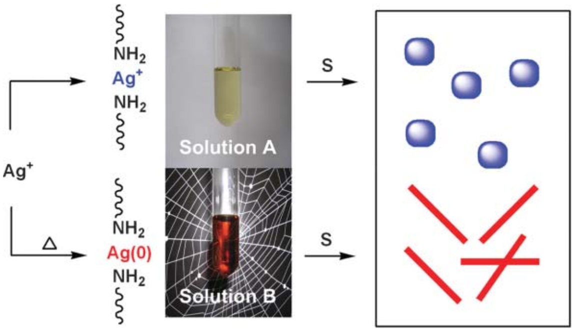

Fig. 2 Illustration of the origin of the mixed-shape problem.

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solution **A** changed its color from yellow to red (solution **B** in Fig. 2). In a careful investigation, it was observed that the color started to redden at 169 °C.

Next, we performed a diverse series of experiments to obtain information on the chemical species in each precursor solution. It can be postulated that the different colors result from different coordination numbers of cationic silver. It has been reported that silver(I) complexes in crystal structures usually have three a coordination number of 2, 3 or 4, and that their most common coordination number is 4.[9] To characterize the coordination number of the silver complex, we performed fast atom bombardment (FAB) mass spectroscopy. Interestingly, the patterns of the mass spectra of the two precursor solutions were nearly the same. The main peaks appeared at *m*/*z* 374.2 ($AgC_{18}NH_{37} - H$), which implies the coordination of one oleylamine molecule to one silver atom. Unfortunately, the possible larger mass peaks due to the coordination of further oleylamine ligands could not be detected due to the mass spectroscopy detection limit. Thus, we replaced oleylamine with octylamine, having a shorter alkyl chain, to induce a suitably low mass value. As expected, the same color change from pale yellow to red was observed upon heating the octylamine solution (Figs. 3a and 3b). The mass spectra of the silver complexes obtained from the yellow and red precursor solutions showed nearly the same mass pattern as that observed in the case of oleylamine. The main peaks appeared at *m*/*z* 236.4 ($AgC_8NH_{19} - H$) and 365.3 ($AgC_{16}N_2H_{38} - H$). There were no detectable peaks at *m*/*z* 494.6 ($AgC_{24}N_3H_{57} - H$) or 623.8 ($AgC_{32}N_4H_{76} - H$).

Thus, it was concluded that the silver complexes in the yellow and red solutions in Figs. 3a and 3b may have two coordinating ligands. The silver complexes could be isolated by the addition of excess ether, which resulted in the precipitation of a white crystalline solid. From the ^1H NMR spectrum, the existence of octylamine in the precipitates could be confirmed (see the ESI†). The fact that two amine ligands are coordinated to silver was confirmed by the elemental analysis of the silver complex (see the ESI†). Considering that the mass spectrum of the chemical species showed nearly the same pattern, it is believed that the silver complexes in the yellow and red solutions may have the same coordination number. Thus, we speculated that the colors may come from different oxidation states of the silver.

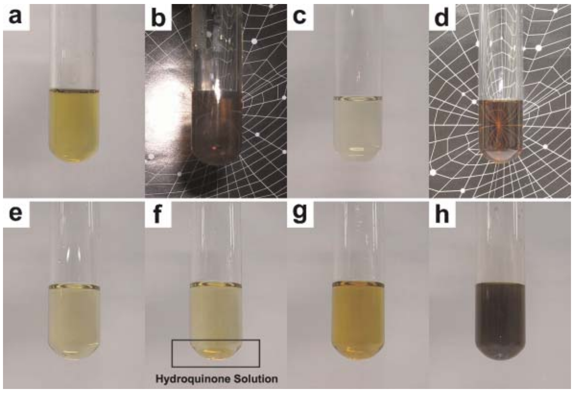

Fig. 3 (a/b) Reduction of cationic silver to zerovalent silver by heating in octylamine, (c/d) by adding $NaBH_4$ in oleylamine and (e–h) by adding a hydroquinone solution in oleylamine.

It has been reported that various amines can reduce cationic gold ions *via* electron transfer from amine to metal in nanoparticle synthesis to form zerovalent gold according to the following equation.[10]

$$Au^{3+} + 3NR_3 \rightarrow Au^0 + 3NR_3^{+\bullet}$$

After preparing precursor solution **A**, having the pale yellow color, we added the well-known reductants sodium borohydride and hydroquinone, which resulted in a change of color to red, as shown in Figs. 3d and 3g. When the red colored solution was left to stand for 12 h and quenched with excess methanol, some precipitates were obtained. The powder X-ray diffraction pattern of these precipitates showed that metallic silver was present (JCPDS 04-0783, see the ESI†). Considering these observations, it was concluded that the red color resulted from zerovalent silver.

According to this observation, we tried to prepare uniform-shaped anisotropic silver sulfide nanomaterials.[11] When precursor solution **A** was injected into a solution of sulfur in 5 mL of oleylamine at 100 °C and stirred for 5 h, cubic nanoparticles with an average size of 28.5 nm were obtained. Fig. 4a shows a TEM image of the synthesized silver sulfide nanoparticles. The high resolution TEM (HR-TEM) image shows that the synthesized nanoparticles had good crystallinity (Fig. 4b). Energy dispersive X-ray spectroscopy (EDS) analysis showed that the stoichiometric ratio of silver to sulfur was 2 : 1 (see the ESI†). The powder X-ray diffraction (XRPD) pattern of the synthesized cubic nanomaterials (in the middle of Fig. 5c and ESI†) shows the enhanced intensity of the ($\bar{1}12$) and (022) crystalline planes, which supports the uniformity of the shape.[12] Prolonging the reaction time from 5 to 13 h did not have any significant influence on the size and shape of the nanoparticles. In contrast, the reaction of solution **B** with sulfur in 5 mL of oleylamine at 100 °C for 5 h produced one-dimensional silver sulfide nanorods with an average width of 15.5 nm (Fig. 4d).

The nanomaterials that formed during the first hour were also one-dimensional nanorods (Fig. 5a). The low magnification TEM image in Fig. 5a confirms the homogeneity of the shape of the nanorods. Also, the intensity of the peaks for the (111) and (121) crystalline planes in the top XRPD pattern (JCPDS 14-0072,

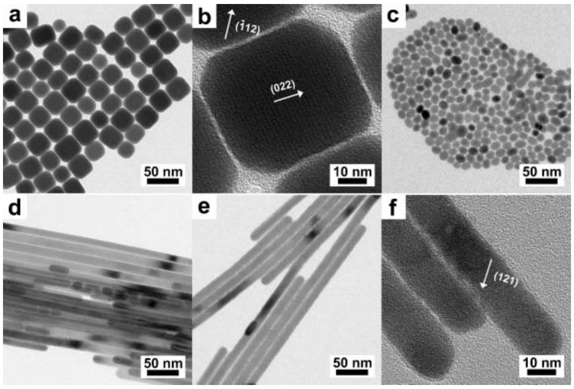

Fig. 4 (a) TEM and (b) HR-TEM images of silver sulfide nanoparticles obtained using precursor solution **A** at 100 °C for 5 h. TEM images of silver sulfide nanomaterials obtained using precursor solution **B** at 100 °C (c) immediately, (d) for 5 h, (e) for 13 h and (f) HR-TEM image of nanowires.

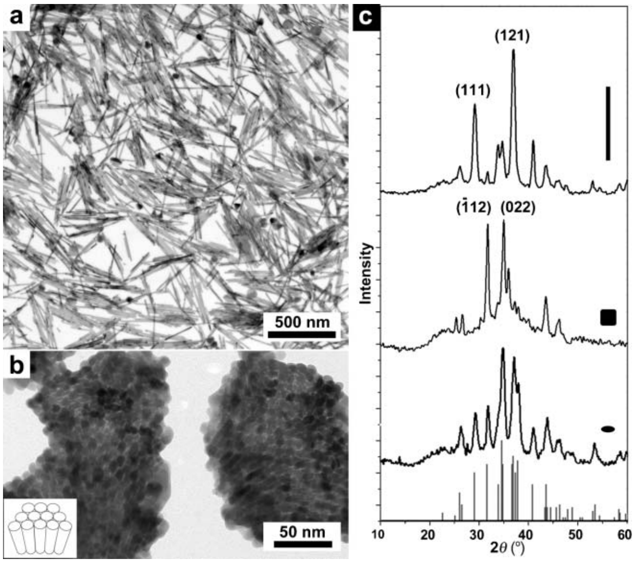

Fig. 5 (a) Low magnification TEM image of nanorods obtained using precursor solution **B** for 1 h. (b) TEM image of silver sulfide nanorods obtained by reacting precursor solution **B** with one equivalent of sulfur at 100 °C for 1 h. (c) XRPD patterns of silver sulfide nanorods in Fig. 4d (top), nanocubes in Fig. 4a (middle) and nanoparticles in Fig. 4c (bottom).

acanthite having a monoclinic crystal system) of Fig. 5c is enhanced. Fig. 4e shows that nanowires formed after 13 h. In the low magnification image, the attained lengths of the nanowires were several micrometers. It was found that the length of the one-dimensional silver sulfide nanorods could be controlled by changing the concentration of sulfur. For example, when the number of equivalents of sulfur was reduced from 5 to 1, the length of the one-dimensional silver sulfide nanorods was reduced to 100 nm, which therefore have a relatively small aspect ratio ($\sim$4).[13] Interestingly, these short nanorods showed an interesting self-assembly behavior, as shown in Fig. 5b and Fig. S5†. Upright-arranged nanorods were observed over almost the entire region of the grid. To obtain information on the early stages of nanowire growth, we quenched the reaction mixture immediately after the injection of solution **B**. Fig. 4c shows the TEM image of the spherical-like nanoparticles that were obtained. Thus, it can be concluded that metal sources of different oxidation state can have different reactivities in the growth of nanomaterials; the cationic silver complex can be used as a precursor to obtain isotropic growth, while the zerovalent silver complex can be used to obtain anisotropic growth in order to form one-dimensional materials. Recently, it has been suggested that these two pathways might be involved in the synthesis of lead chalcogenide nanoparticles, which involves the reaction of a cationic metal source with a sulfur source and the reaction of zerovalent metal with a sulfur source.[14]

In conclusion, the origin of the mixed-shape problem in the shape-controlled synthesis of silver sulfide nanomaterials was investigated. Amine reduction during the dissolution of silver nitrate can generate zerovalent silver species. It was reasoned that zerovalent and cationic silver species might have different reactivities in the growth of silver sulfide nanomaterials, and that this might be the origin of the mixed-shape problem in their synthesis. One-dimensional silver sulfide nanocrystals were successfully prepared using the reduced silver precursor solution. This work provides two valuable lessons in the synthesis of semiconductor nanomaterials. Firstly, the chemical reactions that are susceptible to occur during the dissolution of the precursor are not innocent in the shape-controlled preparation of nanomaterials, but may be a critical factor in the mixed-shape problem and should therefore be taken into consideration when trying to understand and control the resultant shape. Secondly, changing the oxidation state of the precursor by appropriate heating in an amine solution can provide new opportunities for the shape evolution of nanomaterials. We believe that the observations made herein could be extended to the shape-controlled synthesis of a diverse range of metal chalcogenide nanomaterials.[15]

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